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Energy transfer in $\text{LiCaAlF}_6\text{:Ce}^{3+}$

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Abstract

Time-resolved X-ray excited luminescence, induced absorption and thermostimulated luminescence in pure and Ce-doped LiCaAlF_6 crystals have been investigated. It was found that the Ce-doped samples have a fast rise time and a 25 ns decay time following pulsed photoexcitation and a 6 ns rise time and a 50 ns decay time following pulsed X-ray excitation. This may be connected with the transport and sequential capture of charge carriers at or near the Ce^{3+} ion. The overlapping self-trapped exciton emission (280 nm) and Ce^{3+} ion absorption (270 nm) bands also makes excitonic energy transfer possible. Shallow and deep traps were found in the $\text{LiCaAlF}_6\text{:Ce}^{3+}$ crystals.

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1. Introduction

It is known that scintillation light yield, rise time, and decay time depend strongly on the dominant mechanism of the energy transfer from the matrix to the emission centers [1]. In particular, trapping of charge carriers can give rise to the slow component in luminescence kinetics that restricts the time resolution of scintillators based on 5d–4f radiative transition in Ce^{3+} ions [1,2].

The physical processes associated with scintillation rise times and decay times were investigated earlier using ultrafast measurements of luminescence following pulsed X-ray excitation [3,4]. Measurements of the scintillation rise time in a

variety of materials provided information about energy transfer mechanisms, including ultrafast (<30 ps) creation of hot holes and excitons, prompt (<100 ps) sequential hole–electron capture, and delayed (10 ns) sequential electron–hole capture at an activator site. If the self-trapped exciton (STE) emission overlaps the absorption band of an activator, resonant energy transfer can also occur. A slow (~10 ns) rise time component due to STE- Ce^{3+} transfer was found for the fluoride scintillator crystals BaF_2 [5] and LiYF_4 [4].

It was shown recently that for X-ray excitation, Ce-doped LiCaAlF_6 (LiCAF) crystals exhibit intense ultraviolet emission characteristics of Ce^{3+} ions and with a short decay time [6]. Thus, this material is useful as a scintillation detector. Energy storage was also found in irradiated crystals at room temperature.

This paper is devoted to the study of energy transfer in LiCAF:Ce crystals.

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2. Experimental

Pure, Ce-doped, and Ce,Na-codoped LiCAF crystals were grown by the Czochralski technique in a CF_4 atmosphere [7]. The experimental set-ups for absorption, emission, and thermostimulated luminescence measurements are described in Ref. [8]. The scintillation rise times and decay times were studied using a pulsed X-ray system having a time resolution of ~ 60 ps [3].

3. Results

Decay curves of the 5d–4f emission for a LiCAF:Ce crystal following pulsed X-ray and photoexcitation are shown in Fig. 1. For X-ray excitation, there is a distinct rise time $\tau_r \sim 6$ ns; therefore a delay in energy transfer from the matrix to the Ce^{3+} emission center is observed. In addition, the decay time is increased to 50 ns. In contrast, for photoexcitation, a fast rise time and a monoexponential decay time of 25 ns following direct excitation in the spectral region of the 4f–5d transition of Ce^{3+} was observed [9].

Absorption, photo- and radioluminescence spectra of pure and Ce-doped LiCAF at room

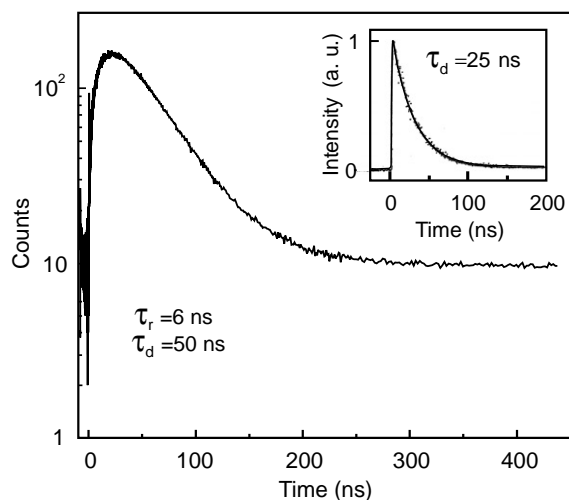


Fig. 1. Decay curve of the 5d–4f Ce^{3+} emission following pulsed X-ray excitation of LiCAF:Ce. Inset: Decay curve of the 5d–4f Ce^{3+} emission following direct photoexcitation of LiCAF:Ce [7].

temperature are presented in Fig. 2. In pure LiCAF, an intrinsic UV-luminescence band with maximum at 280 nm and half-width ~ 0.67 eV appears at temperatures below 200 K. This emission is most likely due to the self-trapped exciton in LiCAF. The STE emission is weak in Ce-activated samples and strongly overlaps the Ce^{3+} ion absorption band. The Ce^{3+} luminescence intensity is essentially independent of temperature in all the ranges investigated (up to 550 K). The temperature dependence of STE yield in pure LiCAF is shown in Fig. 3 (curve 1). Differential curve (2) demonstrates that the decrease in luminosity with increasing temperature is maximal near 160 K. The activation energy is estimated to be 0.36 eV. The thermostimulated luminescence peak associated with the delocalization of V_k centers was found at this temperature.

Irradiation-induced absorption spectra for pure and Ce-doped crystals are shown in Fig. 4. The main wide band at 262 nm in the undoped sample corresponds to F-center absorption. F-center and Ce^{3+} bands overlap strongly. The Ce^{3+} ion absorption band is lowered significantly under irradiation. F-coloration in Ce-containing crystals

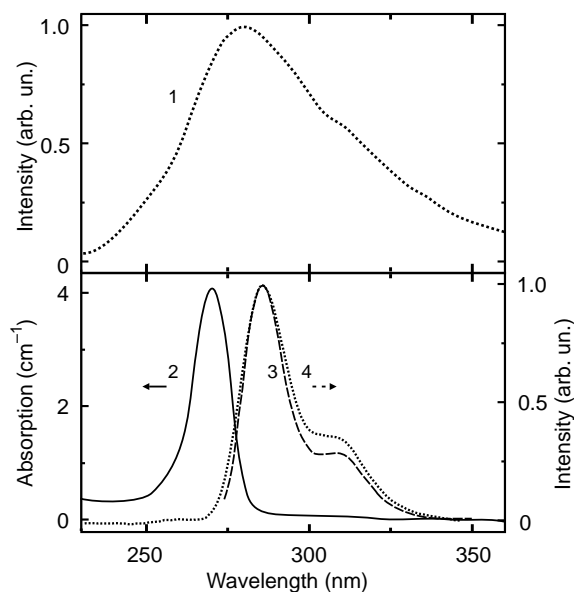


Fig. 2. X-ray excited luminescence of pure LiCAF at 150 K (1). Absorption (2), photo (3) and X-ray (4) excited luminescence of LiCAF:Ce at room temperature.

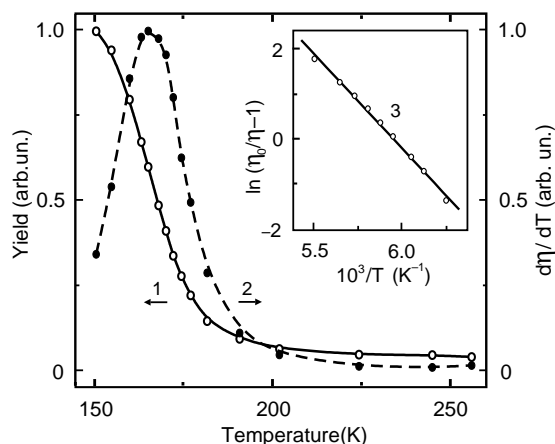


Fig. 3. Temperature dependence of STE yield (1), (3) and differential curve (2) for X-ray excitation of pure LiCAF crystal.

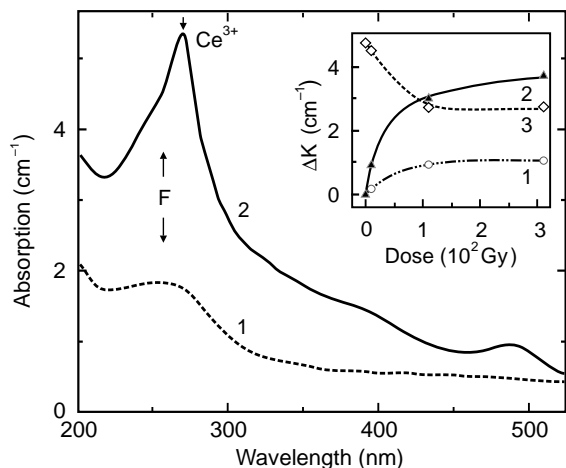


Fig. 4. X-ray-induced absorption in pure (1) and Ce-doped (2) LiCAF crystals. Dose 300 Gy. Inset: Dose dependencies of F band formation in pure (1) and Ce-doped (2) samples; Ce^{3+} absorption band decreasing (3) in LiCAF:Ce.

is far greater than in the undoped crystals. Some additional weak absorption bands were found in the range of 380–490 nm in activated samples.

F-center absorption decreases in two-steps: at 330–380 K and at 500–580 K. In the latter temperature region, the Ce^{3+} absorption increases (Fig. 5A).

As it was shown in Ref. [6], Ce-containing crystals exhibit afterglow immediately after high-dose irradiation at room temperature. This in-

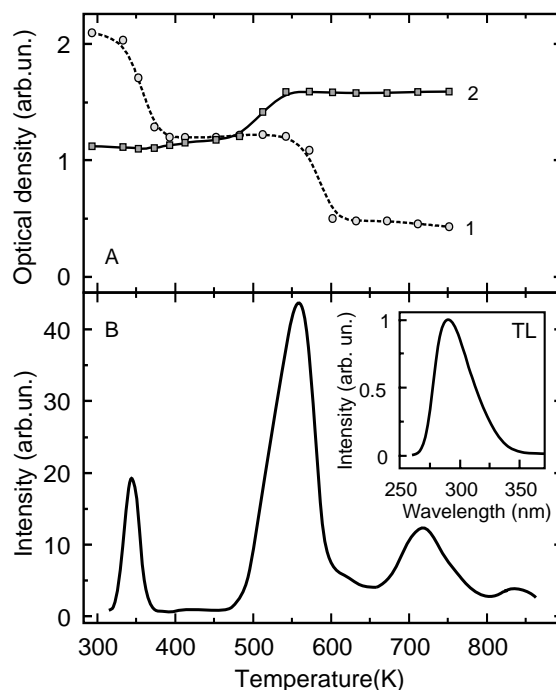


Fig. 5. (A) Temperature dependence of F-center (1) and Ce^{3+} (2) absorption bands for LiCAF:Ce irradiated at room temperature. (B) Glow curve of LiCAF:Ce. Dose 0.5 Gy. Heating rate 0.2 K/s. Inset: Thermoluminescence spectrum at 550 K.

dicates that some traps release charge carriers in this temperature region. The main peak of thermostimulated luminescence is at 550 K with the typical for Ce^{3+} ion emission (Fig. 5B).

4. Discussion

The increase in decay time with X-ray excitation (50 ns) relative to direct photoexcitation in Ce^{3+} at the absorption band (25 ns) suggests the presence of shallow traps in LiCAF:Ce.

The presence of a rise time in X-ray excited emission suggests some mechanisms of energy transfer from matrix to the Ce^{3+} ion. Direct electron capture at Ce^{3+} ions seems to be unlikely because the Ce^{3+} ion is known to be a typical hole trap. One would expect electron capture at anion vacancies, forming F-centers, and hole capture by fluoride anions, forming V_k centers. Thermal diffusion of a V_k center along the matrix to an

F-center will lead to the creation of a STE. If the STE arises in the vicinity of the Ce^{3+} ion, the transfer rate can be high. If the STE forms somewhere else, it will have to diffuse to the neighborhood of the Ce^{3+} luminescence center. Resonant exciton energy transfer to the activator ion may then occur because of STE emission (280 nm) and Ce^{3+} absorption (270 nm) bands overlap strongly in LiCAF:Ce.

Note that the introduction of Ce^{3+} into the matrix at Ca^{2+} sites is accompanied by the formation of charge-compensating defects: V_{Li}^- , $(\text{Li}_{\text{Ca}}^+)^-$ in LiCAF:Ce and $(\text{Na}_{\text{Ca}}^+)^-$ in LiCAF:Ce, Na. Such defects may act as hole traps. For electrons captured at anion vacancies, the tunneling of electrons to hole centers could lead to activator ion excitation and luminescence.

These results show intense afterglow, thermally stable intrinsic and activator color center generation, and high-temperature thermostimulated luminescence in high-dose irradiated LiCAF:Ce crystals at room temperature. All of these suggest the presence of deep traps in Ce-doped samples. These traps have lead to the μsec afterglow in irradiated LiCAF:Ce scintillators, described in Ref. [6].

5. Conclusions

The present study of energy transfer mechanisms shows the presence of shallow and deep intrinsic traps in pure LiCAF crystals and

activator traps in Ce-doped crystals. The rise time of the scintillation pulse in LiCAF:Ce may be connected with the sequential electron–hole recombination of carriers, captured directly at Ce^{3+} ion or/and at the point defects. In addition, the overlap of the STE-emission and the Ce^{3+} absorption bands indicates a high possibility of resonant excitonic energy transfer.

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